# SUMMARY OF QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) REQUIREMENTS

A QA/QC system involves a systematic set of procedures, checks, audits, and corrective actions intended to ensure that all design, performance, environmental monitoring and sampling, and other technical and reporting activities related to achieving project related FFMS data quality objectives are met. Chapter 8 identifies and describes the steps in designing and executing QA/QC procedures for a FFMS sampling and analysis program.

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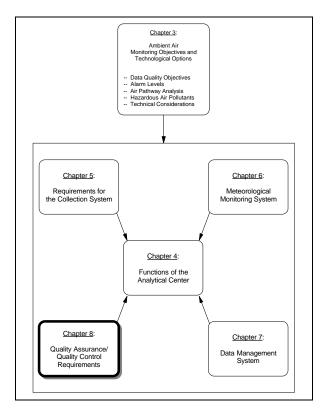
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#### 8-1. Introduction

The QA/QC program for the FFMS involves a systematic set of procedures, checks, audits, and corrective actions to ensure that all design, performance, environmental monitoring and sampling, and other technical and reporting activities for achieving the project DQOs are met. Important components of the QA/QC planning process involve developing a clear understand of how the data will be used, defining the DQOs that are needed to ensure project success and establishing how data quality will be assessed. These and other QA/QC components are incorporated into the project's SAP, which is composed of two parts: the FSP and the QAPP.

Although QA and QC are both intended to provide for the production of quality data, the two concepts are fundamentally different in several regards. Quality control involves those controls and checks that are *routinely implemented by project staff* to maintain the integrity of the collected data. An example of a QC activity is the periodic calibration of an instrument as specified in the operating manual. In contrast, QA is a quality auditing function *performed occasionally by individuals external to the project team.* An example of a QA activity is the review of instrument calibration records to ensure that the calibrations have been performed correctly. For USACE projects, the QA and QC requirements may be project and/or contract specific or may otherwise default to ER 1110-1-263, EM 200-1-6 or other specified USACE guidelines.

#### 8-2. Quality Planning

Quality planning is an integral part of the USACE's environmental programs, as addressed in EM-200-1-2 and should include FFMSs, when applicable, activities at HTRW sites. That EM provides project planning guidance to develop data collection programs and define DQOs for HTRW sites. The use of that manual as part of the quality planning of a project is intended to promote the identification of the type and quality of data required for HTRW site cleanup, progressing from site investigation and evaluation through remedial design and site close-out for USACE customers.

That EM-200-1-2 describes a four-phase data quality design process. The four phases are:

- Phase I Identify project strategy.
- Phase II Determine data needs.
- Phase III Develop data collection options.
- Phase IV Design data collection program.

Consistent with the philosophy described in EM 200-1-2, the design, installation and utilization of FFMSs at HTRW sites also requires technical project planning.

The most important step in designing and executing a fixed fenceline monitoring program at a HTRW site is the initial planning that takes place at the very beginning of the project. The extra effort put into this initial planning more than pays for itself in improved data quality and reduced rework. The essential elements of the initial planning process are discussed below and summarized in Figure 8-1.

a. Intended use of the data. The design of a FFMS for monitoring at HTRW projects can contain numerous deficiencies when there is poor understanding of the intended use of the data. When this deficiency occurs, the data collected do not address the needs of the program, and the resources that were devoted to the data collection effort may have been wasted. Thus, the first step in the initial planning process is to clearly define how the data will ultimately be used and to reach agreement concerning this use among all involved parties.

Agreement on the total intended uses of data is not always straightforward, especially where there may be multiple uses and differing priorities among the effected parties. If the data are to be used for risk assessment purposes, for example, a number of potentially hazardous air contaminants may need to be measured and instrument detection limits set at very low limits. Alternatively, if the data will be used to demonstrate compliance with air emission standards, an entirely different set of sampling and analysis requirements are involved.

For most USACE projects involving FFMS, the data collection efforts will typically support on-site remediation activities. *Pre-remediation* air quality monitoring may be conducted to establish background concentrations and site-specific meteorology to gain experience with the sampling and analytical methods to be used later in the project. Monitoring during the *remediation* phase generally has two objectives: (1) documenting any air quality impacts associated with the remediation activities and (2) triggering corrective actions in the event of an air contaminant release above a predetermined level, as discussed in Chapter 4. *Post-remediation* sampling may be conducted to confirm that air contaminant levels have returned to baseline levels and that any air quality impacts occurring during remediation have been eliminated. Given the diverse and complex data collection needs involved with a remediation project, the intended use of the data must be firmly established as a first step in the project planning process.

- b. Data quality objectives. As discussed in Chapter 3, determining DQOs is also an essential step in the planning process. Once the DQOs have been established, it is possible to select those sampling and analysis procedures that will provide the required quality of data. Additionally, later in the project, the quality of measured data can be assessed by determining if the DQOs have been achieved.
- c. Field Sampling Plan. Not until the intended use of the data and the project DQOs have been clearly established can the FSP be prepared. A depiction of the FSP and QAPP and their general contents is shown in Figure 8-1. The FSP specifies the sampling and analysis methods and procedures to be used and contains a number of elements that are crucial to achieving the desired levels of data quality. These elements include chain of custody procedures, sample packaging and shipping requirements, contractor quality control procedures, and a corrective action plan. Additionally, the FSP should reference or append SOPs (see Appendix C) for the selected sampling and analysis methods. For most on-site equipment operation and sampling procedures, these SOPs should be prepared specifically for the methods and site specific applicability. For USACE, projects, a required FSP should contain the required SOPs and should be reviewed and approved during the preparatory phase of the USACE three phase control system.
- d. Quality Assurance Project Plan. The final step in the initial planning process is preparing the QAPP. The required elements of a QAPP are summarized in Figure 8-2. For FFMSs, the QAPP should include reference and audit sample analysis. Especially important are the sample custody and holding time requirements, calibration procedures and frequencies, internal QC checks, calculation of data quality indicators, and corrective actions. Additionally, the QAPP identifies the project's QA Officer, who officially approves and implements the QAPP. A QAPP review and approval checklist from EM 200-1-3 is presented in Figure 8-3.

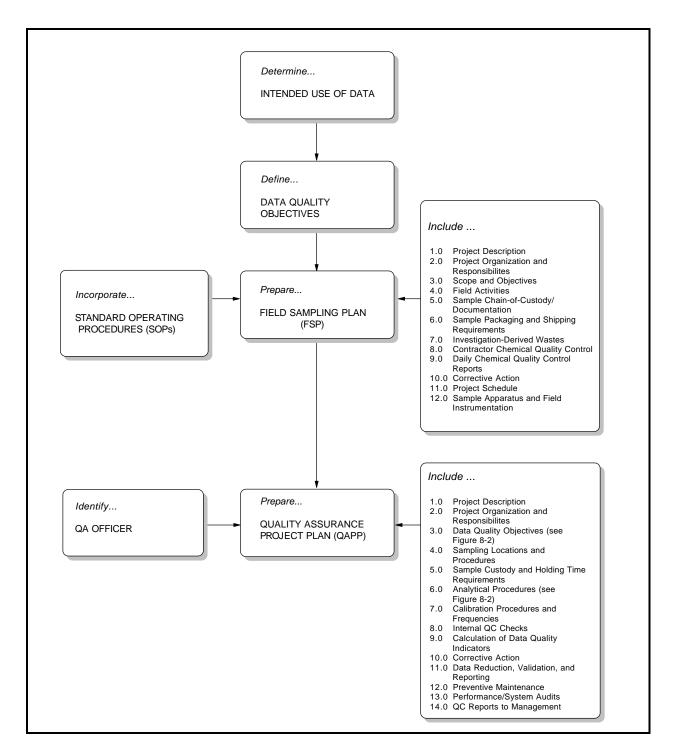


Figure 8-1. Example of essential elements of quality planning as part of a HTRW FFMS.

- Title Page. Should include the name of the document and the date it was prepared. The QA officer should sign the title page, ensuring that field and laboratory personnel are aware of the requirements for precision, accuracy, completeness, representativeness, and comparability.
- Table of contents. Includes a listing of the QAPP elements and any appendices, figures, and tables. A list of the recipients of official copies of the QAPP should also be provided.
- Project description. Consists of a general paragraph describing the scope of work, general objectives, and required measurements. (If the project description is discussed in the field sampling plan, it does not need to be repeated in the QAPP.)
- Project organization and responsibility. Identifies key field and laboratory personnel or organizations that are necessary for each analytical activity during the study. A table or chart showing the organization and lines of authority should be included. The organizational chart should also include all subcontractors and their key points of contact. The QA officer should be organizationally independent of project management so that the risk of conflict of interest is minimized.
- Data quality objectives (see Figure 8-1). Describes the QA objectives for the data so that the data can achieve their intended use. Project-specific data quality objectives that have been identified for the project, short-term decisions that will be made during the project planning phase, and long-term decisions that will be made prior to project closeout should be highlighted.
- Sampling locations and procedures. References the sections of the field sampling plan that discuss the general rationale for choosing sampling locations and the sampling procedures proposed for each matrix.
- Sample custody and holding times. References the appropriate sections (e.g., sample custody/ documentation) of the field sampling plan for all custody and holding requirements pertaining to the field and laboratory activities.
- Sampling and analytical procedures. (See Figure 8-1) Identifies the appropriate sampling and analytical test methods that should be used for each environmental sample. The field sampling plan can be referenced.

- Calibration procedures and frequencies. Discusses the calibration procedures to be used, the number and concentration of calibration standards, and the calibration range and procedures to establish and verify the calibration of instruments.
- Internal QC checks. Identifies the specific internal QC methods to be used, including analyses of method blanks; use of laboratory control samples, and use of environmental samples as duplicates, matrix spikes, and duplicates.
- Calculation of data quality indicators.
   Discusses how precision, accuracy, completeness, representativeness, and comparability goals are to be calculated from the project data.
- Corrective actions. Addresses corrective actions that must be implemented if QA specifications are not met. Corrective actions could include resampling, reanalyzing samples, or auditing laboratory procedures. Persons responsible for initiating these actions should be identified.
- Data reduction, review, validation, and reporting. Discusses the data review process that is required to assure the validity of the data. Data reduction procedures should be summarized and the persons responsible for data reduction identified. The format for reporting the data and the data reporting schedule should be specified.
- Preventive maintenance. Discusses the preventive maintenance plan that will be implemented to minimize downtime of field and laboratory instrumentation.
- Audits. Describes the performance, systems, data quality, and management audits that will be performed onsite and at the laboratory.
- © *QC reports to management*. Discusses QC reports that will be prepared. These reports typically include an assessment of accuracy, precision, completeness, representativeness, and comparability; audit results; and significant QA problems encountered.

# Figure 8-2. Example of required elements of a quality assurance project plan (QAPP) for a HTRW FFMS.

	surance Objectives		
(This in specificatio	formation should be referenced to the Project Work Plan or contract		
'а.	Are field measurement objectives discussed?	Y	N
	analytical method detection limits defined?	Y	N
N/A c. Are	quality control parameters defined?	Y	N
N/A	Precision and accuracy	Y	
N/A	_		N
2. N/A	Completeness	Y	N
3.	Representativeness	Y	N
N/A 4.	 Comparability	Y	N
N/A	_		
	stody/Documentation		
	field logbook maintained with appropriate information concerning ing/sampling?	Y	N
N/A	nethod of identifying photographs discussed?	Y	 N
N/A			
c. Is s N/A_	ample numbering system appropriate?	Y	N
1. N/A	Project designator	Y	N
2.	Location designation	Y	N
N/A 3.	Matrix code	Y	N
N/A 4.	Sample sequence numbers	Y	N
N/A 5.	Depth interval (if required)	Y	N
N/A d.			
u. 1.	Sample Documentation  Does information on sample label include:		
	Site name N/A	Y	N
	b Identification of sample station number	Y	N
	N/A  Date and time of collection	Y	N
	N/A Name of sampler	Y	N
	N/A		
	<ul> <li>Analytical analyses requested N/A</li> </ul>	Y	N
	Media sampled N/A	Y	N
	Preservation method	Y	N
2.	N/A Are completed custody seals required over sample container		
N/A	(except VOA) lids?	Y	N
3.	Does chain-of-custody record contain appropriate information? N/A		Y
N 4.		Y	N
N/A	_		

Figure 8-3. Example of a QAPP review and approval checklist from EM 200-1-3.

# PERFORMANCE **EVALUATION AUDITS**

**TECHNICAL** 

SYSTEMS AUDITS

reference material is disguised so that the operator or analyst will treat it no evaluation usually involves the program to be subjected to a

precision of the measurement What were the accuracy and

whether problems present during testing may lead to erroneous results. Often, the collection of data is facilitated with the aid of

is likely to be adequate for the intended use of the data, or

operating within the established

provides a simple format for documentation, but also provides an indication of whether the auditor has examined all elements of the

system under evaluation.

A checklist not only

checklists.

## MANAGEMENT SYSTEMS AUDITS

nal management systems necessary for the successful implementation of are designed to answer the following found. Management systems audits existence and adequacy of the interprimary purpose is to determine the has been institutionalized within an a quality assurance program. The extent to which quality assurance actions to correct any deficiencies An on-site audit of an organization's quality assurance management system used to verify the organization and to recommend questions:

recording and transfer of raw data, data calculations, the documenta-

terize data quality. This assessment involves a detailed review of the

tion of procedures, and the selection and discussion of appropriate data quality indicators. A data quality audit answers the following questions:

tion of all procedures used in the data collection effort to allow the repetition of the effort by a person

Is there sufficient documenta-

qualifications similar to those of the original data collector?

or team with technical

Is there sufficient document-

assessment of the methods used

to collect, interpret, and report the information required to charac-

- Does the organization maintain official position descriptions for all QA personnel and provide for a the organization identify the specific role of quality assurance in its operations? Does the management policy of
  - quality assurance program that includes appropriate milestones and documentation of specific Is it possible to identify specific resources that were allocated to the management of the work assignments?

sufficient information presented to enable potential users to evaluate the limitations of the data and to determine whether the

intended use of the data is appropriate?

ation to verify that the procedures specified for use in the data collection effort were properly followed?

- mining the status of documents o organization's QA program?

  Does the QA Officer maintain an activities required of individual adequate system for deter-
- and is there evidence of a routine concern for QA in organization activities? projects?

  Is there adequate training in QA,

performance audit, it is more common for only the critical, or most important, measurements to be evaluated. The measurement or analysis of a reference material having associated with it a known value or composition. It is important that the value or composition or the reference material be certified, or at least verified, prior to use, and that the certification or verification be adequately documented. Usually, the identity of the differently from a test program sample

A performance evaluation audit will

DATA QUALITY AUDITS

> measurement system. Although it is possible for each measurement of a test A quantitative evaluation of a

answer the following questions:

- system at the time of the audit?

  Do the quality control data collected during routine system operation correctly reflect data quality?

  Is the measurement system
- If the results of previous audits are available, has data quality significantly changed?

The result of the audit help determine whether the data collection efforts need modification and if the quality control procedures are

recordkeeping, data validation, operation, maintenance, calibration, reporting, and quality control procedures. Since the above items

tion of a measurement system used to assess and document all facilities, equipment, systems,

A qualitative on-site evalua-

should be defined in the approved QAPP, the QAPP provides the basis for the audit. During the

audit, any undocu-

Figure 8-4. Example of four types of quality assurance audits associated with a FFMS at a HTRW site

Although quantitative information is not provided, the audit helps the auditor quickly determine whether the data quality

from the approved QAPP are cited and noted in the audit report. mented or unauthorized deviations

- ☼ Background (upwind) samples. Samples similar to the sample under investigation, but outside the presumed area of contamination. These samples are taken to measure the concentration of analytes considered naturally occurring, due to another contaminant source, or due to the media used in sample acquisition.
- □ Trip Blanks. Whenever the possibility exists for accidentally adding extraneous material into the sample during collection, shipment, or analysis, a trip blank sample should be used to assess the magnitude of this contamination. Blank samples associated with the field sampling effort include both field blanks and trip blanks.
- Field Control Samples. General term assigned to field-generated replicates (duplicates/splits/spikes), blanks, background/upwind samples, etc., associated with reference method monitoring (RMM).
- Field QA. A sample that is a collocated replicate of a field sample, except that the sample is sent to the USACE's QA laboratory for analysis; allows early detection of sampling, documentation, packaging, shipping, and analytical errors.
- Field QC Sample. A field replicate (duplicate) sent blindly to the laboratory; results assess sampling precision and handling techniques.
- - <u>Laboratory Control Sample/QC</u> <u>Reference Sample</u>. A spiked blank sample

prepared by the analyst (preferably obtained from an outside source) which combines a portion, or all, of the elements being analyzed; used for calculation of precision and accuracy and to verify that the analysis is under control.

<u>Laboratory Duplicate Samples</u>. Identical splits of individual samples that are taken and analyzed by the laboratory to assess method reproducibility.

Matrix Duplicate/Laboratory Duplicate (DUP). Two representative aliquots of the same sample matrix subjected to identical analytical procedures to assess the procedural precision of the method through the calculation of relative percent difference (%RPD).

<u>Method Blank</u>. The use of extraction solution, zero air, and adsorption media prepared in the same manner as samples; used to determine if cross contamination or memory effects are present.

Surrogate Compounds/System Monitoring Compounds. Brominated, fluorinated, or isotopically labeled compounds (not expected to be detected within environmental samples) which are added to every field sample; used to evaluate sampling and analytical efficiency by measuring recovery.

<u>Trip Blank</u>. Trip blanks are transported with empty sample containers to the HTRW site and remain sealed until analyzed with collected environmental samples. Trip blanks permit evaluation of contamination generated from sample containers or occurring during the shipping and laboratory storage process.

Figure 8-5. Example of typical QC samples associated with a FFMS.

The QAPP also identifies the QA audits to be performed during the sampling and analytical phases of the

project. Audit results are very important because they can identify problems before it is too late to implement corrective actions. Additionally, audit results provide validation of the quality of data being collected. The four types of QA audits associated with a FFMS are summarized in Figure 8-4. For FFMSs, audits should address sample collection, system performance and analytical procedures and data analysis.

#### 8-3. Characterizing Data Quality

A QC program makes use of a variety of QC samples and data quality indicators to assist in characterizing the quality of data collected. The types of QC samples used in the field will depend upon the nature of the data collection effort, but will likely include field replicates (duplicates, splits, and/or field spikes), field blanks (zero air, canister, and/or trip blanks), and background (upwind) samples. Laboratory QC procedures will usually include the analysis of replicates, standards, reference material, surrogates, and/or RAM spiked samples. These and other types of QC samples associated with a FFMS program are defined in Figure 8-5. For FFMSs, sampling and analysis may involve the Analytical Center and/or reference method monitoring (RMM). For the FFMS perimeter air monitoring program, prescribed data quality qualifiers are defined in terms of precision, accuracy, completeness, representativeness, and comparability. These data quality indicators can then be compared against the project DOOs to determine whether these aspects of the FFMS project's data quality needs have been met. Each of the five data quality indicators are described below.

a. Precision. Precision examines the distribution of measured values about their mean. The distribution of measured values refers to how different the individual measured values are from the average reported value. Precision may be affected by the natural variation of the matrix or contamination within that matrix as well as by indeterminate errors made in field and/or laboratory handling procedures. For chemical analysis of environmental samples, precision is commonly determined from duplicate sample analyses and expressed as relative percent difference (RPD), as follows:

RPD (%) = 
$$\left[ \frac{|C_1 - C_2|}{\overline{C}} \right] \times 100$$

where:

 $C_1$  and  $C_2$  = absolute value of the difference of the observed values.

 $\overline{C}$  = the mean of the duplicate values [ $(C_1 + C_2)/2$ ].

For continuous monitors for which collocated sampling is not practical, precision is determined by the measurement of a certified gas. For these measurements, precision is calculated as follows:

RPD (%) = 
$$\left[ \frac{X_1 - X_2}{X_2} \right] \times 100$$

where:

 $X_1$  = measured value as documented by real-time, on-line analytical system in the Analytical Center.  $X_2$  = certified value as documented by manufacturer certificate.

If sufficient replicate samples are taken (usually at least eight), precision can be estimated as the Relative Standard Deviation (RSD) or the Coefficient of Variation (CV), as follows:

$$CV = RSD = \left(\frac{S}{\overline{C}}\right) \times 100$$

where:

CV = coefficient of variation.

RSD = relative standard deviation.

S = standard deviation.

 $\overline{C}$  = mean value of replicate observed values.

$$S = \left[\frac{1}{n-1} \sum_{i=1}^{n} (C_i - \overline{C})^2\right]^{\frac{1}{2}}$$

where:

 $\frac{C_i}{C} = \frac{1}{C}$  observed value of the ith replicate.

n = number of replicates.

and the mean,  $\overline{C}$ , is defined as:

$$\overline{C} = \frac{1}{n} \sum_{i=1}^{n} C_i$$

For a perimeter real-time, on-line volatile organic analytical system in the Analytical Center, precision is measured daily by challenging the system with a known reference gas or individual organic compounds and calculating the system RPD.

b. Accuracy. Accuracy measures the bias in a measurement system. Sources of bias may include the sampling process, field contamination, preservation methods, handling, sample preparation, and analysis techniques. Field equipment blanks and trip blanks can help assess the potential contaminant contribution from various outside sources. Analytical accuracy can be assessed through the use of known and unknown QC and spiked samples and is commonly represented as percent recovery (%A) or percent bias. Accuracy of a realtime, on-line volatile organic analytical system is determined by collocating a reference method or Compendium method sampling system (i.e., RMM) with the real-time system and calculating:

$$\%A = 100 \text{ x} \left[ \frac{X_u}{X_s} \right]$$

where:

 $X_S$  = measured value as determined by the reference method monitoring (RMM)/Compendium method monitoring.

 $X_U$  = measured value as determined by the real-time gas chromatographic system in the Analytical Center

c. Completeness. Completeness is defined as the percentage of measurements made that are judged to be valid measurements compared to the total number of measurements planned. Specified levels of overall completeness, in addition to particular completeness goals for critical samples, should be established as part of the project DQOs. Percent completeness (%C) is calculated as follows:

$$\% C = \left[ \frac{V}{N} \right] x \ 100$$

where:

V = number of measurements judged to be valid, as measured by the real-time monitoring system.

N = number of valid measurements needed to achieve a specified statistical level of confidence (i.e., 80%).

Overall completeness accounts for both sampling and analysis completeness, each of which may be specified separately. Valid samples include those analytes in which the concentration is determined to be below detection limits. There may also be different completeness goals for various parameters and time periods. Typically, completeness is expressed as overall completeness for a given parameter at a given site for a specified period, such as a year or the duration of monitoring. Typically, overall completeness goals of 80 to 90 percent for real-time monitoring data and greater than 90 percent for meteorological and RMM data should be readily available.

d. Representativeness. Representativeness expresses the degree to which sample data accurately and precisely represent (1) the characteristics of a population of samples, (2) parameter variations at a sampling point, or (3) environmental conditions. Representativeness is generally a qualitative parameter that is most concerned with proper siting and design of the sampling program. It can be accessed qualitatively or through the use of duplicate field and laboratory samples, which provides both precision and representativeness information.

Typically, for real-time FFMSs at HTRW sites, one or more locations may be chosen to represent background concentrations, short-term maximum exposures, long-term maximum exposures, worker exposure, or average concentrations at or downwind of the site. Meteorological data such as temperature, humidity, wind speed, direction, and precipitation should be reviewed to see if locations actually met the characteristics expected based on earlier modeling. A failure to achieve required representativeness with a FFMSs is generally the result of either system design or system operation failures.

*e. Comparability*. Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. For example, sample data should be comparable with other measurement data for similar samples and sample conditions. Comparability is achieved by using compatible procedures to collect and analyze representative samples and to report analytical results in appropriate units.

#### 8-4. QA/QC Applications to FFMS Programs

Although specific applications of QA/QC will vary among HTRW sites, a number of considerations are common to all FFMS projects. These considerations are discussed below, along with some recommendations and areas of concern.

- a. Data Quality Objectives. The determination of DQOs will depend upon specific project needs. For the monitoring methods described in this EM, representative and achievable data quality indicators have been identified that will be appropriate for most applications. These are listed in Table 8-1. It is recommended that a table similar to Table 8-1, but with a column added that compares the DQOs with measured data quality indicators, be included in the SAP and each monthly HTRW project progress report.
- b. Sampling site location. Sampling equipment needs to be located where representative samples can be collected. For most HTRW FFMS programs, representative sampling sites should be selected to assess (1) any increase in emissions from the HTRW site during remediation and (2) potential exposure to workers and nearby residents. Obviously, a critical factor in site selection should be wind direction. Although sometimes airport wind data can be relied upon, in most situations the airport is too far away to take into account local terrain and other factors (e.g., nearby buildings) that can affect localized wind speed and direction. Thus, it may be desirable to set up a meteorological station on site to establish prevailing wind direction. Depending on the duration and season of the sampling event, the meteorological station may need to be operated for an extended period of time (several months to a year) to determine representative conditions; or it may be necessary to operate the meteorological station for the duration of the project and select sampling locations based on this on-line information. Another site selection factor involves the location of potentially exposed workers and nearby residents (e.g., monitors may need to be set up between the emission source and these potentially exposed individuals).
- c. Internal QC. Table 8-2 presents examples of the QC checks that are appropriate for the types of instrumentation described earlier in this EM as part of a HTRW FFMS program. Additionally, blanks involving one clean sampling device (e.g., a PUF/XAD-2 adsorbent cartridge, glass fiber filter, or SUMMA canister) should accompany a certain percentage of the samples to the field and back to the laboratory to serve as trip and field blanks. The average amount of analyte found on the trip blank should be compared with the amount found in the actual samples; if the trip blank level is greater than 25 percent of the sample amounts, the data should be identified as suspect. During a specified number of sampling events at least one set of collocated samples using RMMs (two or more samples collected simultaneously) should be collected. If agreement between collocated samples is not within  $\pm 40$  percent, the reason for non-agreement should be investigated.
- d. Performance and systems audits. Example performance audits for the types of instruments described earlier in this EM as part of a HTRW FFMS program are presented in Table 8-3. This table is intended to be representative of audits that might be performed; however, additional and/or different performance audits may be needed, depending upon the specific equipment in use. The frequency of performance audits will depend on the intensity and duration of the sampling effort. Systems audits should be performed immediately before the sampling effort begins and again shortly after it begins (e.g., during the first week). Thereafter, systems audits should be performed as often as practicable. Table 8-4 documents the criteria and limits for the performance and system audits involving an HTRW FFMS program.

Table 8-1
Example Data Quality Indicators and Specifications for a FFMS Program at a HTRW Site

Measurement	Accuracy or Recovery (%)	Precision (RPD)	Completeness (%)
Real-time Monitoring Instrumentation			
Analytical system for RAM NMOC	±40	±30	>80
Analytical system for speciated organics	±40	±30	>80
Contingency analytical system for RAM and speciated organics	±40	±30	>80
Time-Integrated Monitoring Instrumentation			
High-volume (HV) TSP/metals	NA	±30	>90
PM <sub>10</sub> /TSP sampling	±0.5 mg	NA	>90
TSP/PM <sub>10</sub> /metal analysis	60-120	<30	>90
Semi-volatile sampling and analysis	60-120	<30	>90
Organic sampling and analysis	60-120	<30	>90
Meteorological Monitoring			
Wind speed	±0.2 m/s	NA	>90
Wind direction	±5°	NA	>90
Temperature	±0.5°C	NA	>90
Barometric Pressure	±0.5 in Hg	NA	>90
Relative humidity	±5%	±30	>90
Precipitation	±0.25 in H <sub>2</sub> O	±30	>90

NA = not applicable.

As an additional tool for system audit, many USACE HTRW programs have specified the use of one or more mobile sampling station to be used as a data quality indicator. These stations are generally configured to be mobile units which can be collocated with any of the FFMS sample inlets or other perimeter or off-site monitoring stations for making simultaneous measurements. This approach allowed any problems with the stationary monitoring stations or FFMS sample and transport to be quickly detected. It also allows for additional precision calculations for the measurement system.

e. Preventive maintenance and corrective action. Many of the problems that occur during field sampling programs can be avoided with proper maintenance. Table 8-5 presents an example of a routine/preventive maintenance schedule for the equipment typically used during a HTRW FFMS program. Note that some maintenance procedures must be performed daily, whereas others are performed just twice a year. All preventive

Table 8-2
Example of QC Checks Associated with HTRW FFMS Program

QA/QC Sample Type	Suggested Minimum Frequency	Responsible Party	Application
FIELD			
Collocated samples for TSP/PM <sub>10</sub> semi-volatiles and volatiles	10% of sampling events	Field crew	Used to determine variation due to sample collection and/or ambient conditions
Flow checks of samplers (single point)	All sampling events; must be within 10% of desired flow rate.	Field crew	Used to verify initial flow point calibration curve to laboratory standard curve
Sampler certification	Once per quarter	Field crew	Used to verify that sampler is not contaminated
Retention time (RT) check for real-time analytical system for 3-5 indicator organic compounds	Daily	GC operator	Used to verify that retention time differences for speciated organcis do not exceed 0.5 minutes from initial check
Single-point calibration check for real-time analytical system for 3-5 indicator organic compounds	Daily	GC operator	Used to verify calibration check for speciated organics do not exceed ±25% of initial calibration
Multi-point calibration check for real-time analytical system for 3-5 indicator organic compounds	Weekly	GC operator	Used to verify proper operation of GC system
RAM NMOC calibration at 1 ppm for real-time analytical - system	Daily	GC operator	Used to verify proper operation of GC RAM system, within ±10% of standard
Heated sample lines efficiency verification with 1 ppm NMOC and 100 ppb of 3-5 indicator organic compounds	Initially, quarterly	GC operator and field crew	Used to verify transfer efficiency of the heated sample lines extended out to 1,000 feet.
LABORATORY			
Field blank for canister, PUF/XAD-2 adsorbent and filters	Method dependent, typically not less than 5% of trip numbers	Field crew	Used to detect contamination during field operations and shipping
Trip blank for canister, PUF/XAD-2 adsorbent and filters	5% of trip numbers (0 if field blank used in lieu of trip blank)	Field crew	Used to detect contamination during shipping
Lot blank	1 per event per lot, 3-6 whenever new lot of adsorbent acquired	Laboratory	Used whenever manufacturers supply a lot of samplers or when a fresh lot of sampling media is cleaned
Reagent/method blank	1 per reagent blank per batch	Laboratory	Used for solvent desorbed sorbent media
Surrogate spike	Every sample when used (semi-volatile only)	Laboratory	Used to verify that bias results are not being reported high or low due to problems with a specific analysis.

Table 8-3	
Example of HTRW FFMS Program Performance A	udits

Instrument	Type of Performance Audit	Frequency	Criteria
Analytical system from NMOC/ speciated organics	Flow audit of extractive system heat trace sample lines	Quarterly	±10% of set-point
Times, specialed organics	Chemical audit of extractive system heat trace sample lines     1 ppm NMOC gas     Indicator organic	<ul><li>Quarterly</li><li>Quarterly</li></ul>	±40% of accepted value ±40% of accepted value for individual analytes
	Compounds     Leak check     (positive/negative)	<ul> <li>Quarterly</li> </ul>	
Heat-trace lines	<ul><li>Flow audit check</li><li>Leak check</li></ul>	<ul><li>Quarterly</li><li>Quarterly</li></ul>	±10% of set-point
Time-integrated and collocated samples	<ul><li>Flow audit check</li><li>Leak check</li></ul>	<ul><li>Quarterly</li><li>Quarterly</li></ul>	±10% of set-point
Meteorological station	<ul><li>Wind direction check</li><li>Wind speed check</li></ul>	<ul><li>Quarterly</li><li>Quarterly</li></ul>	Wind direction: ±5° Wind speed: ±0.2 m/s
Data acquisition system	Electronic Voltage Check	• Weekly	±10% of set-point

Table 8-4
Example of Criteria and Data Qualifier Limits for a FFMS Involving Real-Time, Perimeter Air Monitoring

Criteria	Limits
Quantitative Measurements	
Replicate precision	±30%
Audit accuracy	70-130% of accepted value
Data completeness	80%
Qualitative Measurements	
Representativeness	Documented
Comparability	Documented

maintenance actions must be documented for later review by a QA auditor. A plan for initiating and implementing corrective action should be developed, specifying: (1) conditions that will require corrective actions; (2) personnel responsible for initiating, approving, implementing, and evaluating the resolution of corrective actions; and (3) specific corrective action procedures to be used when predetermined control limits are exceeded. Corrective actions are usually instrument-specific, and equipment manuals and EPA-approved standard operating procedures should be consulted for guidance. In general, it is appropriate to initiate corrective actions when the following conditions occur:

• When predetermined acceptance standards are not attained (e.g., objectives for precision, accuracy, and completeness).

- When sampling procedures or data compilation techniques are determined to be faulty.
- When faulty equipment or instrumentation are found.
- When samples and test results cannot be traced with certainty.
- When quality assurance requirements have been violated.
- When required approvals have not been obtained.
- When system and procedure audits indicate problems.
- When the results of management assessment indicates problems.
- When a laboratory/inter-laboratory comparison study result indicates problems.

All routine maintenance activities should be documented on a form such as the example provided as Figure 8-6. Such records must be traceable to the specific equipment item. These records will be subject to audit by USACE's designated project QA personnel. Preventative maintenance and corrective action activities should also

be documented in the instrument log book, site log books, and daily reports.

*f. Special concerns.* No matter how good a QA/QC program is, unexpected challenges will still occur. Several lessons learned from earlier fenceline monitoring projects include the following:

- Set-up and troubleshoot the complete system prior to field deployment
- Have all system plans and specifications available on-site and reviewed by an electrical engineer prior to the start of the monitoring program.
- Keep in mind that monitoring projects are not research projects; you do not have the luxury of trial and error.
- Make sure all systems can "talk" to each other.
- Know what has to be reported (including units) and develop appropriate reporting forms.
- Build contingency costs into cost estimates to address unexpected QA/QC problems.

USACE HTRW FFMS EQUIPMENT MAINTENANCE/REPAIR REPORT		
Instrument/Equipment Item:	Date:	
Description of Problem:		
Action(s) Taken:		
Date/Time Item Returned To Service:		
	Initials:	

Figure 8-6. Example of maintenance/repair report form as part of a HTRW FFMS program.

Table 8-5
Example of Typical Routine/Preventative Maintenance Activities Associated with HTRW FFMS Program at a HTRW Site

Equipment/Instrument	Activity	Frequency
Inlet probes	Perform flow check Replace filter cartridges	Monthly Monthly
Heat trace sample lines	Perform flow check Determine line temperature Inspect and clean electrical junction boxes Inspect and replace fuses	Weekly Weekly Annually As needed
Sample intake manifold system	Disconnect individual lines and blow clean w/ compressed air Lubricate valves	Monthly Monthly
Sample conditioning system	Inspect and clean sample dryer Remove, inspect, clean and test gas cylinder regulators Check performance of perma-pure dryer	Annually Annually Semi-annually
Analytical system for RAM NMOC	Remove, inspect, clean and replace lamp Measure voltages at detector	W eekly W eekly
Analytical system for speciated organics	Remove, inspect, clean and replace lamp Measure voltages at detector	W eekly W eekly
Data acquisition system	Remove housing, blow circuit boards clean w/ compressed air Inspect power cord	Annually
	Inspect external port connections and linkages Replace fuses	Annually Annually Annually
Printers	Remove and inspect ink cartridge	Weekly
External alarm & pager system	Replace fuses	Annually
Telephone/fax/modem system	Inspect com port connections Inspect cords	Annually Annually

With regard to specific equipment, prior projects indicate that the following concerns are common to many HTRW real-time, on-line FFMS projects:

#### **Heat-Trace Lines**

- Provide a "reliable" source of power (power interruptions are common).
- Carefully evaluate the temperature control system prior to field deployment, to verify that it can maintain a constant temperature.
- Provide access to all line components so that the temperature of segments can be monitored.
- Provide security for lines and voltage points.
- Test the probe filter with target compounds prior to installation.

• Verify the cleanliness of the sample transfer lines prior to installation.

#### **Meteorological Station**

- Use a software package that is consistent with the reporting requirements.
- Determine the method for calculating stability classification prior to field deployment of the meteorological equipment.
- Know all of the required reporting units (i.e., Langleys, mbars, etc.).

#### Real-time Analytical System in Analytical Center

- Set up the screen display so that the elapsed chromatography time is shown; this way, the user knows where he is in the cycle for individual analyte determination.
- Ensure that all systems in the Analytical Center (i.e., DAS, meteorological, analytical) can "talk" to each other prior to field deployment.
- Keep in mind that compliance, not science, is required; do not turn the project into a research project.
- Become very familiar with the software package prior to running the system.

#### **Data Acquisition System**

- Keep in mind that repairs usually include changing the electronic chips; extra chips should be kept on- hand.
- Perform test calculations prior to field deployment.
- Incorporate proper "averaging" times consistent with contract specifications.
- Understand the "short falls" of the system and be prepared to work around them.

### 8-5. Generation of Standard Test Atmospheres

a. Introduction. As new and improved real-time, on-line analytical systems for monitoring VOCs at HTRW sites have developed, it was imperative that these systems could be field calibrated and audited so the data generated would achieve project required objectives. As a result, more emphasis has been placed on the development of technology for the field generation of test calibration gases for field calibration and audit purposes. This calibration and audit technology can be used to ensure that data generated is an accurate representation of the pollutant concentration being monitored.

Due to deterioration (electrical or mechanical), environmental effects and site activities, measurement monitors and apparatus designed to operate within a specific range of conditions are subject to unforeseen changes which may affect the data generated by the monitors. To continually evaluate the performance of a real-time system, known concentrations of the target analytes should be used to challenge the system. The response of the monitors to the known concentration is used for system evaluation and the calculation of the precision of the system, as discussed in Paragraph 8-3.

The technologies available for generating known concentrations of target analytes for precision calculations can be divided into two broad categories:

- Dynamic calibration systems.
  - gas cylinder dilution system (e.g., concentrated cylinder gas followed by a series of dilutions)
  - permeation systems
  - flash vaporization
  - water purge
- Static systems.
  - static dilution
  - high pressure gas cylinders

In considering these two categories for generating known concentrations of test atmospheres, the part per billion [ppb] to parts per million [ppm] concentration ranges for the target analytes are the highest priority. Attempts to prepare static standards in fixed volume containers and in flexible bags may be impossible. Such features as adsorption, absorption, stability, and other concerns must be considered. Dynamic calibrations overcome many of the inherent problems of static systems; but dynamic calibrations are not without their drawbacks. Traceability, stability, availability of standards, etc. are just some of the limitations associated with dynamic calibrations. The purpose of this section is to discuss the methods available for generating known standards of target analytes using both static and dynamic systems so that calibrations and precision calculations can be performed.

- b. Generating standard test atmosphere using static dilution system.
- (1) Cylinder gas concentration. The gas cylinder is probably the best example of a static calibration system. The cylinder can be made of different materials and produced in different sizes. The use of gas cylinders to generate a test atmosphere has been well established in FFMS programs. Highly accurate gas standards for such pollutants as SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, CO, NMOC, and speciated organics have been used routinely for calibration of FFMSs. Manufacturers supply gas mixtures with a certification of analysis and a statement of accuracy. Accuracy levels are generally quoted between 2 to 5 percent of the component values.

Gas cylinders come in different sizes, materials of construction, and weights. The contents of gas cylinders can be limited by the material of construction. Multiple gases are frequently incorporated into one cylinder. Inclusion of multiple analytes in one cylinder is greatly dependent upon their reactivity, compressibility, and stability.

Cylinders intended to contain specified pollutant gases mixtures are produced by adding a known volume of gas to the cylinder, then pressurizing the cylinder with a diluent gas to a total gas cylinder pressure. The concentration of the target analyte in the gas cylinder can be calculated by the following equation:

$$C_{ppm} = \frac{10^6 \text{ x } V_c}{V_a + V_c} = \frac{10^6 P_c}{P_t}$$

$$C_{\%} = \frac{10^2 \times V_c}{V_a + V_c} = \frac{10^2 P_c}{P_t}$$

where:

 $C_{ppm}$  = final concentration of analyte in gas cylinder, ppm.

 $C_{\%}$  = final concentration of analyte in gas cylinder, %.

 $V_c = volume of analyte gas in the cylinder, L.$ 

 $V_a = volume of diluent gas added to the cylinder, L.$ 

 $P_c$  = pressure of analyte gas in the cylinder, mmHg.

 $P_t$  = final pressure of gas mixture in the cylinder, mmHg.

This technique of producing gas concentrations is fairly accurate for concentrations from 10 ppb to more than 6,000 ppm, depending on the stability of the gas mixtures.

Another technique of preparing cylinder standards is "by-weight." During this process, the cylinders are evacuated, then filled to a weight and allowed to reach equilibrium with the target analyte. The cylinder is then filled to a final weight with diluent gas. All weighing is performed on a high precision balance. The final concentration is determined by the weight percent of target analyte in the gas mixture.

- (2) Cylinder gas problems. Gas manufacturers have documented numerous problems associated with maintaining accuracy of prepared certified gas standards. The problems which have been documented and investigated and can be categorized as:
  - Cylinder material related.
  - Gas stability related.
- c. Cylinder material. The material of construction plays an important part in the long-term stability of target analytes (i.e., VOCs, NMOC) in gas cylinders. When reactive gases such as oxides of nitrogen, carbon monoxide, or sulfur dioxide and volatile organics are blended in a steel cylinder with an inert balance gas, the concentration can vary with time, temperature, and pressure. The mixture's instability is random and dependent on the condition of the individual cylinders. It has been documented that the instability is a function

of gas absorption or reaction with the cylinder walls. Gas cylinders were initially constructed of mild steel and consequently lacked long term stability. To alleviate this problem, many manufacturers have provided gases in materials of construction other than mild steel, including stainless steel, aluminum, and treated cylinders.

The following factors affect the stability of standards in pressurized cylinders:

- Contamination.
- · Reaction.
- Absorption.
- Adsorption.

Another method of decreasing the reactivity between the target analyte and cylinder material is to "soak" the cylinder with a high concentration of the gas of interest.

The theory behind this "soaking process" is that, with time, all of the gas that is going to react with or be absorbed into the cylinder walls will do so during the conditioning period. When the cylinder is put into its final mixing stage, any further reaction or absorption is supposedly precluded.

This method of preconditioning has met with only limited success for volatile organics. When the pressure or temperature of the cylinder changes, the gas that was absorbed during the soaking process can desorb; therefore, the concentration that the cylinder delivers can actually increase.

- d. Cylinder gas stability. Gas stability is one of the most serious problems associated with certified standards. Gas stability is defined as the ability of a gas mixture to maintain its original concentration with time, temperature and cylinder pressure. Many volatile organics, such as alcohols, esters, ethers, alkenes, etc., are unstable at very low concentrations (<50 ppb) in gas cylinders. The instability is due to:
  - Reaction with moisture.
  - Reaction with other trace gas impurities.
  - Reactions with cylinder walls.

The stability of several criteria pollutants (SO<sub>2</sub>, CO, NO, CO<sub>2</sub>, NMOC, etc.) has been well documented.

The stability of VOCs in compressed gas cylinders is dependent on the particular hydrocarbon for which a standard is needed. In general, the more reactive hydrocarbons are less stable.

- Relatively less stable: Aromatics and oxygenated or halogenated hydrocarbons.
- Relatively more stable: Propane, butane, hexane, and methane.

Volatile organics that are stable in gas cylinders for 6 months at the 50 ppb level are listed in Table 8-6.

Table 8-6 Volatile Organics that are Stable for 6 Months in Gas Cylinders at the 50 ppb Level				
<ul> <li>vinyl chloride</li> <li>vinylidene chloride</li> <li>chloroform</li> <li>1,2-dichloroethane</li> <li>benzene</li> <li>toluene</li> <li>Freon 12</li> <li>methyl chloride</li> <li>1,2-dichloro-1,1,2,2-tetrafluoroethane</li> <li>hexachloro-1,3-butadiene</li> <li>methyl chloroform</li> <li>carbon tetrachloride</li> <li>cis-1,3-dichloropropene</li> <li>trans-1,3-dichloropropene</li> <li>ethyl benzene</li> <li>o-xylene</li> <li>m-xylene</li> <li>p-xylene</li> </ul>	<ul> <li>1,1,2,2-tetrachloroethane</li> <li>1,3,5-trimethylbenzene</li> <li>1,2,4-trimethylbenzene</li> <li>m-dichlorobenzene</li> <li>o-dichlorobenzene</li> <li>p-dichlorobenzene</li> <li>1,2,4-trichlorobenzene</li> <li>methyl bromide</li> <li>ethyl chloride</li> <li>Freon 11</li> <li>dichloromethane</li> <li>1,1-dichloroethane</li> <li>cis-1,2-dichloropropene</li> <li>1,2-trichloroethane</li> <li>1,2-trichloroethane</li> <li>1,2-trichloroethane</li> <li>tetrachloroptopane</li> <li>1,2-tirchloroethane</li> <li>tetrachloroethylene</li> <li>chlorobenzene</li> </ul>			
<ul> <li>styrene</li> </ul>	benzyl chloride			

- *e. Cylinder gas certification techniques.* Presently, several types of gas standards are available from the NIST and commercial manufacturers. They are:
  - NIST--Standard Reference Materials (SRMs).
  - Gas Manufacturers Primary Standard (GMPS).
  - Gas Manufacturers Certified Reference Materials (CRMs).
  - Unanalyzed gases.

The NIST-SRMs are sold by the NIST as primary standards. These standards are prepared gravimetrically

Table 8-7. Gas Standards Tolerances			
Gas standard	Tolerance percent (%) of the component		
NISTSRMs	±1		
GMPS CRM	±1 ±3		
Unanalyzed GMCSs	±15 ±1 of SRM		

on a high load, high sensitive balance, with a tolerance of ±1 percent of the component. GMPSs are traceable to NIST-SRMs and are used to calibrate instruments used in certifying Gas Manufacturer's Certified Standards (GMCSs). The GMCS are prepared by a variety of gravimetric and pressure-volume temperature techniques and analyzed by instrumentation that has been calibrated by NIST-SRMs or GMPSs. These standards normally have a certification tolerance of ±3 percent. The unanalyzed standards are normally prepared in

the same manner as the GMCSs, but are not analyzed. Their certification tolerances are normally  $\pm 15$  percent. For some HTRW projects, site-specific reference materials or custom ordered mixtures may be necessary. Table 8-7 summarizes the gas standards available and their associated tolerances.

(1) NIST SRMs. Standard Reference Materials have been characterized by the NIST for some chemical and physical properties and are issued with a Certificate that gives the results of the characterization. These results are obtained by one of the three methods of certification, including using (1) a previously validated reference method; (2) two or more independent, reliable measurement methods; or (3) a network of cooperating laboratories, technically competent and thoroughly knowledgeable with the material being tested.

The SRMs are defined as being well-characterized and certified materials. They are prepared and used for three main purposes: (1) to help develop accurate methods of analysis (reference methods); (2) to calibrate measurement systems used to facilitate the exchange of goods, institute quality control, determine performance characteristics, or measure some property at the limit of the state-of-the-art; and (3) to assure the long-term adequacy and integrity of quality control processes. In these ways, SRMs help ensure the compatibility and accuracy of environmental measurements.

NIST has offered SRM materials, such as "Ambient Toxic Organics in Nitrogen," SRM No. 1804. For a real-time, on-line volatile organic FFMS, the SRM would be used as an independent audit of the system on a semi-annual or annual basis. The limited use of the SRM is due to its high expense and limited availability.

(2) Certified Reference Materials. The SRMs and CRMs are gaseous standards developed by the NIST in cooperation with the EPA. The main objective of this program was to help supply gaseous standards to industry without depleting the SRM stock. The NIST could neither increase production nor allow "out-of-stock" situations to develop with their SRM inventory. Consequently, a method was developed that enabled the specialty gas industry to produce accurate gas standards while maintaining traceability to NIST-SRMs. The new CRMs duplicates SRMs in stock according to stability, homogeneity, and concentration.

Manufacturers generally certify CRMs by analyzing their concentrations with an analyzer that has been calibrated with SRMs. The idea is to calibrate the analyzer with two or three SRMs, then analyze a "batch" of CRMs with the calibrated analyzer. This process provides traceability to NIST-SRMs and increases the number of reference gases available for commercial usage.

- f. Generating standard test atmospheres using gas cylinder dilution system
- (1) Introduction. One of the simplest and most economical systems for providing a known concentration of target volatile organic analyte to a FFMS or analytical system is the single gas dilution system. A simple dilution system involves mixing a gas of known concentration of target analyte with a contaminant-free diluent gas to provide a known concentration of gas of lesser value than the original. By measuring the volumetric flowrates of each gas stream (see Figure 8-7) and knowing the concentration of the original gas to be diluted, one can calculate the final concentration with the following equation:

$$C_{u}Q_{u} = C_{d} (Q_{u} + Q_{d})$$

where:

 $C_u = concentration of undiluted pollutant gas provided by manufacturer (usually a CRM), ppm.$ 

Q<sub>u</sub> = volumetric flow rate of undiluted pollutant gas, mL/min.

 $C_d$  = final concentration of diluted gas, ppm.

 $Q_d$  = final volumetric flow rate of the diluent gas, mL/min.

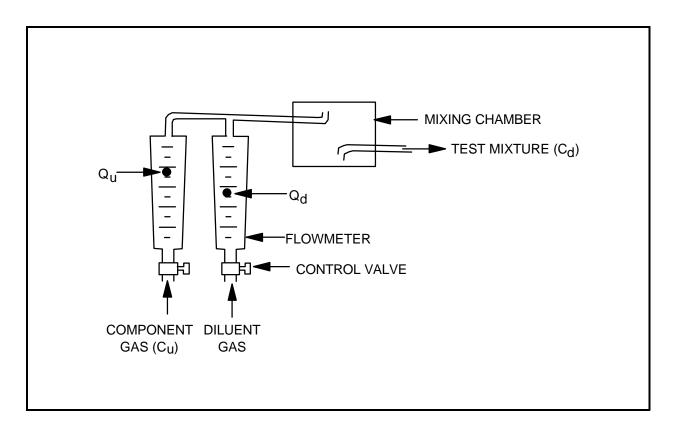


Figure 8-7. Example of gas dilution system using a single gas cylinder diluted with zero air as part of a HTRW FFMS program.

From the above equation, the following variables must be accurately measured to determine the final concentration:  $C_u$ ,  $Q_u$ , and  $Q_d$ . Knowing these three values and rearranging the above equation, the final concentration of the diluted pollutant gas can be calculated with the following equation:

$$C_{d} = \frac{C_{u}Q_{u}}{Q_{u} + Q_{d}}$$

This procedure is the most common technique to produce low concentration standards of gaseous volatile organics from a higher gas concentration.

#### (2) Flow Measuring Devices

Three common methods for measuring flows in a gas dilution system are:

- Rotameters.
- Critical orifices.
- Mass flow controllers.
- (a) *Rotameter*. One of the simplest means of measuring volumetric flows involves the use of rotameters. If calibrated, rotameters provide a direct correlation of volumetric flow.

The rotameter consists of a vertically graduated glass tube and a float located in the tapered vertical tube.

In operation, the fluid to be measured passes through the tapered tube, carrying the float to a position in the tub where its weight is balanced by the upward forces to the fluid flowing past it. At this point, a constant pressure differential across the float is reached, which is unique for each rotameter. The forces acting in the upward direction (buoyant and drag force) equal the force acting in the downward direction (gravity).

Most rotameters calibrate at room temperature with the downstream side open to the atmosphere. Correction for temperature and pressure variations from original calibration configuration are made by the following equation:

$$Q_{u} = Q_{s} \left[ \frac{P_{1} \times T_{2}}{P_{2} \times T_{1}} \right]^{1/2}$$

where:

 $Q_u$  = volumetric flow rate of sampling configuration, corrected to present temperature and pressure, L/min.

Q<sub>s</sub> = volumetric flow rate of calibration configuration, L/min.

 $P_1 = pressure$  at original calibration configuration, in Hg.

 $P_2$  = pressure at sampling configuration, in Hg.

 $T_1 =$  temperature at calibration configuration, °R or °K.

 $T_2 =$  temperature at sampling configuration, °R or °K.

Because corrections of this nature are usually cumbersome and inaccurate, rotameters are usually calibrated under sampling configuration.

(b) Critical orifices. Critical orifices have progressively replaced rotameters in monitoring volumetric flow. If operated properly, the critical orifice ensures exact delivery of a gas stream with  $\pm 2$  percent.

The orifice meter consists of some form of restriction located in a tube constructed of glass, metal, or other material. Two pressure taps, one upstream and one downstream of the orifice, serve as a means of measuring the pressure drop. As a fluid traverses the orifice, a pressure drop develops that can be correlated to flow rate.

As the pressure drop across the orifice increases, flow rates increase. The region of the calibration curve whose flow rate changes with pressure drop is termed noncritical flow and is associated with a variable orifice meter. Within this region of the calibration curve, the pressure drop across the orifice should be set to a desired number to generate a known flow.

If the pressure drop across the orifice is increased until the downstream pressure is equal to approximately 0.53 times the upstream pressure, the velocity of the gas stream becomes sonic. Even if the pressure is increased, no increase in flow will occur. The orifice meter has therefore become "critical." Under these conditions, a constant flow will occur as long as the 0.53 pressure relationship exists.

(c) *Mass flow controller*. This device operates on the principle that as a gas passes over a heated surface, heat is transferred from the surface to the gas. The amount of current required to keep the surface at a constant temperature is a measure of the velocity of the gas.

#### 8-6. Reference Methods Requirements for Calculating System Accuracy

As part of a FFMS program, system accuracy of both real-time and time-integrated monitoring systems must be maintained within prescribed limits as defined in the program QAPP. As illustrated in Paragraph 8-2, system accuracy of a real-time, on-line, volatile organic analytical or a TSP/PM<sub>10</sub> system is determined by comparing a RMM (i.e., Compendium method) with the on-site real-time VOC sampling system in the Analytical Center, as defined by the following equation:

$$\%A = 100 \text{ x} \left| \frac{X_u}{X_s} \right|$$

where:

%A = calculated accuracy, %.

 $X_n = measured$  value as a determined by the on-line, real-time analytical system, ppm.

 $X_s =$  measured value as determined by the RMM (i.e., Compendium method), ppm.

For TSP/PM<sub>10</sub> time-integrated monitoring systems, system accuracy is determined by collocating a duplicate sampling system next to the on-site monitor and extracting a representative sample from the same general air parcel at the HTRW site. As specified in Chapter 4, the siting of the second sampler must meet the same monitoring siting requirements as the on-site sample, which are:

- 2-10 meters vertical spacing above ground.
- Unrestricted air flow around the reference method inlet.
- Greater than 2 meters away from the on-site sampler.
- Away from obstructions (i.e., trees, buildings, etc.) by a distance of 10 times the height of the obstacle.

Relative accuracy for real-time, on-line FFMS monitors at HTRW sites, can be determined either by collecting a second split sample at the analytical center, (using such methods as TO-1, TO-2, TO-3, TO-14, TO-15 or TO-17), at the FFMS sample inlet at a perimeter location or by taking a collocated sample adjacent to a sample inlet. The significant difference between the two approaches is that by taking a split sample the sample is assumed to be homogeneous for volatiles whereas collocated samples collected adjacent to a FFMS sample inlet provides a sample which may be a different atmosphere due to the required 2 meter separation from other samplers. The user must review the project DQOs and determine which method is best for the program. Since samples cannot be successfully "split" for particulate matter or a particulate related component such that homogeniety is maintained, collocated samplers are the acceptable compromise.

For real-time volatile organic perimeter air monitoring system, the two compendium methods used as "reference" methods in calculating percent accuracy for a FFMS are generally Compendium Methods TO-14 and TO-15, as previously discussed in Chapter 4 and are briefly reviewed here:

a. Compendium Method TO-14. Compendium Method TO-14 is applicable to specific VOCs at the subppb level that have been tested and determined to be stable when stored in pressurized and subatmospheric pressure canisters. Numerous compounds, many which are chlorinated VOCs, have been successfully tested for storage stability in pressurized canisters. However, minimum documentation is currently available to demonstrate the stability of VOCs in subatmospheric pressure canisters.

Both subatmospheric pressure and pressurized sampling modes are initially used with an evacuated canister and a pump-ventilated sample line during sample collection. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of ambient air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into a pre-evacuated sampling canister.

After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to a predetermined laboratory for analysis. Upon receipt at the laboratory, the canister tag data is recorded and the canister is attached to the analytical system. During analysis, water vapor

is reduced in the gas stream by a Nafion® dryer (if applicable), and the VOCs are concentrated by collection in a cryogenically-cooled trap. The cryogen is then removed and the temperature of the trap is raised. The VOCs originally collected in the trap are revolatilized, separated on a GC column, then detected by one or more detectors for identification and quantification. The analytical strategy for Method TO-14 uses a high-resolution GC coupled to one or more appropriate GC detectors. The recorded values for the speciated organics are then compared to the on-site real-time FFMS to calculate an accuracy value.

b. Compendium Method TO-15. Compendium Method TO-15 is distinguished from Compendium Method TO-14 in that: (1) it addresses a large set of compounds (including polar organics); (2) it uses GC/MS technique as the only means of identifying and quantifying target compounds; and (3) it allows the use of alternative but equivalent methods through performance criteria standards.

In collocating reference methods with inlet probes for real-time monitoring systems, the same siting criteria must be met as locating a single system, as discussed in Paragraph 5-7, and listed earlier in this Paragraph for TSP/PM<sub>10</sub>. They are:



Figure 8-8. Example of collocated time-integrated RMM (TSP and VOC) with perimeter real-time, on-line monitors at a HTRW site

- 2-10 meters vertical spacing above the ground.
- With unrestricted air flow around the reference method inlet.
- No closer than 2 meters to other sampling systems.
- Away from obstructions such as trees, building, etc., by a distance of 10 times the height of the obstruction.

Figures 8-8 and 8-9 document properly collocated sampling equipment at HTRW sites for calculating DQOs associated with accuracy indicators utilizing time-integrated RMM for TSP and volatile organics.

#### 8-7. Corrective Action Requirements

Corrective action procedures should be developed as part of the Project SAP, FSP, QAPP, and SOPs. In the case of instrumentation and equipment, manufacturer's recommendations should be the starting point for all equipment diagnostics, maintenance, and repairs. Corrective action activities recommended as a result of system or performance audits will be recorded in the relevant audit report. In addition, all corrective action activities should also be documented as shown in the example provided in Figure 8-10. These recoeds must also be traceable to the specific equipment or procedural item. Corrective action activities should also be documented in the instrument log book, site log books, and daily reports.

In the event the real-time, on-line FFMS performance conditions are identified as adversely affecting data quality to any significant degree, the cause(s) should be determined and corrective actions taken to prevent reoccurrence. These actions may involve maintenance, repairs, or modifications to instrumentation or equipment and/or modification of operating procedures. Corrective actions may be initiated:

- When predetermined acceptance standards (objectives for precision, accuracy, and completeness) are not attained.
- When data compiled are determined to be faulty.
- When QA requirements have been violated.
- When routine, preventive maintenance activities are required.
- When system and performance audit reports are not acceptable.
- When a management assessment indicates the necessity.
- When required by the result of precision or accuracy comparison studies.
- When samples and test results cannot be traced with certainty.
- When designated approvals have been circumvented.
- When other operating procedures are determined to be faulty.



Figure 8-9. Utilization of RMM, Compendium Method TO-14, in calculating percent accuracy as a collocated unit at the perimeter of a HTRW site.

USACE HTRW FFMS CORRECTIVE ACTION REPORT	
Project I.D.	Date:
Measurement Parameter:	Time:
Description of Problem:	
Recommended Corrective Action:	
Action(s) Taken:	
Date/Time Action Implemented:	
Initials:	

Figure 8-10. Example of corrective action report form as part of a FFMS at a HTRW site.